

Thermal donor formation in CZ-silicon annealed at 450°C in air ambient

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Abstract : Exact kinetics of donor formation and possible number of oxygen atoms in a single thermal donor (TD) are two aspects out of many problems related with oxygen related donors in CZ-silicon, which carry a mark of interrogation. Boron doped *p*-type silicon wafers were annealed in air ambient at 450°C for different durations and subjected to resistivity and FTIR studies. It was observed that ambients do not affect the process of TD generation. Successive increase in annealing times results in the exponential growth of donors with a maximum of $\approx 1.79 \times 10^{17} \text{ cm}^{-3}$ obtained in our samples annealed for 55 hours. Annealing also caused a gradual decrease in absorption coefficient. Maximum observed value of oxygen and carbon precipitations was 2.362 ppma and 1.100 ppma respectively. The diffusion coefficient for oxygen was found to be $\approx 4.17 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$. Oxygen and carbon reduction followed second order kinetics. The activation energy for diffusion of oxygen was found to be $\approx 0.823 \text{ eV}$ and the number of oxygen atoms involved in a single TD formation appears to be seven from our experimental investigations.

Keywords : Thermal donor, annealing, air ambient

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1. Introduction

Czochralski (CZ)-grown silicon (Si) is commonly used in microelectronic devices. It is well known that dissolved oxygen in silicon changes from an electrically neutral state into a shallow donor (the so called thermal donor, TD) by heat treatment around 450°C and this TD disappears by annealing at 500°C. These thermal donors are supposed to be oxygen complexes with an increasing number of oxygen atoms being attached to them during heat treatment. Formation rates of these TDs are strongly dependent upon the processing temperature and upon the concentration of oxygen, typically of the order of $\approx 10^{19} \text{ cm}^{-3}$ in CZ-Si. TDs are generally undesirable because these TDs prevent determination of the quantity of intentionally added dopant. The study of low temperature ($400^\circ\text{C} < T < 500^\circ\text{C}$)

annealing process of CZ-grown silicon is of increasing importance for prospective applications of low temperature cycles to device technologies as well as for fundamental researches on the behaviour of oxygen in silicon.

Even more than four decades of intensive research following their discovery [1], the chemical nature and the atomic structure of oxygen related donors (TDs) are not well understood. TDx^0 ($x = 1 - 11$) and nine singly charged TDx^+ ($x = 1 - 9$) species have been observed in IR spectra [2]. Five new effective-mass-like TDx^0 ($x = 12 - 16$) species have also been observed [3]. These defects are actually with mean activation energies of 0.07 and 0.15 eV for ionisation of charge states [4]. It has recently been established that accelerated diffusion of oxygen impurity atoms occurs in the temperature range 300–500°C corresponding to the formation and thermal stability of oxygen related donors [5].

Infrared (IR) absorption has been a primary integrating tool for oxygen in silicon. Localised vibrational modes for oxygen at interstitial sites in Si introduce a prominent absorption band at 1106 cm^{-1} and 605 cm^{-1} at room temperature respectively. Oxygen aggregate modes for TD defects have been followed from observations that several oxygen atoms are lost from interstitial sites per electrically active donor formed during annealing near 400°C [6]. The intensities for Si–O bands related to aggregates will be weak because only a fraction of the dispersed oxygen precipitate in aggregate formation. Moreover annealing time or temperature to increase the TD concentration introduces a broad spectrum of the TD family members which can cause band overlap and broadening of Si–O absorption bands for the aggregates.

A critical review of the relevant literature reveals that the present state of knowledge on the two issues *viz.* exact kinetics of the TD formation and the number of oxygen atoms involved in a single TD, is still surrounded by an air of uncertainty and one has to go a long way in order to have a widely accepted solution. With this sole motivation, a few results are reported in this article.

2. Material and methods

Czochralski grown boron doped ($B = 0.4 \times 10^{16} \text{ cm}^{-3}$) silicon wafers used in the study were 400–470 μm thick with 80 mm diameter, as cut etched, <100> orientation and resistivity ranging from 80–100 ohm-cm. These wafers were cut down into small pieces of the size $1 \times 2 \text{ cm}^2$ and then subjected to heat treatment in air ambient at a constant temperature of 450°C.

2.1. Resistivity measurement and donor generation :

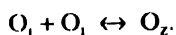
The resistivity of silicon wafer was measured with a collinear four probe array (van der Pauw method) at room temperature and the number of carriers derived from Irvin's curve [7]. Afterwards, the wafer was given desired heat treatment in air ambient and subsequently cleaned in hydrofluoric acid in order to eliminate the surface oxide. The resistivity of the annealed samples was again measured and the corresponding number of charge carriers derived from the Irvin's curve. Assuming that the mobility remains constant,

the difference of the carrier concentration between un-annealed and annealed samples gives the donors generated or annihilated during the heat treatment.

2.2 Oxygen and precipitated oxygen :

Absorption coefficient needed to compute the oxygen content in the samples has been derived from 1106 cm⁻¹ band by FTIR measurements using the procedure laid down by Iizuka *et al* [8]. The value of the absorption coefficient so obtained helped to obtain the interstitial oxygen concentration using the expression $O_i = (3.03 \pm 0.02) \times 10^{17} \alpha_0 \text{ cm}^{-1}$. The initial oxygen concentration in the test wafer was measured without any heat treatment on it. Afterwards, the wafer was given a specific heat treatment and calculated interstitial oxygen concentration. The difference between the two is attributed to precipitated oxygen during heat treatment.

In the low temperature range (< 500°C) the rate of loss of interstitial oxygen (O_i) should be related to trapping of diffusing O_i atoms by other such atoms. O_i dimers are formed in this process.



Assuming that the backward reaction rate is negligible in comparison to the forward reaction rate, the kinetics of O_i loss would be controlled solely by the interaction rate of two randomly diffusing O_i atoms.

$$\frac{d[O_i]_i}{dt} = -8\pi DR[O_i]^2,$$

where, R is the capture radius associated with dimer formation and D is the diffusing coefficient for oxygen. Integrating the above expression, we get

$$\frac{1}{[O_i]_i} = \frac{1}{[O_i]_o} + 8\pi DRt$$

$$\text{or } C(i)^{-1} - C(o)^{-1} = 8\pi DRt,$$

where, $C(i)^{-1}$ and $C(o)^{-1}$ are reciprocal values of oxygen concentration prior to the anneals and after anneals for t time. Plot of $C(i)^{-1} - C(o)^{-1}$ versus time are therefore expected to be linear with a gradient equal to $8\pi DR$.

3. Results and discussion

3.1 Donor generation as a function of annealing time :

Resistivity measurement on the samples annealed for different durations have been performed to ascertain carrier concentration and in turn, donor concentration. Annealing also helped in reducing the inhomogeneities present in the unannealed samples up to a large extent. The resistivity variation as a function of annealing time is shown in Figure 1. The resistivity of the sample annealed upto ≈ 1 hour, increased; but thereafter, for longer annealing period, the resistivity fell off exponentially. This behaviour clearly showed that

p-type sample was converted to *n*-type due to generation of thermal donors [9]. The number of donors generated due to annealing at 450°C is plotted as a function of annealing time in Figure 2. Donor generation was very rapid in the early stages of annealing but decreased

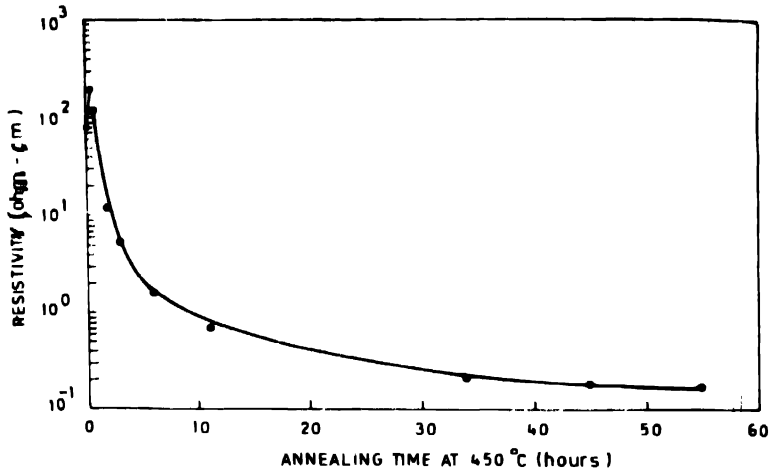


Figure 1. Resistivity vs annealing time at 450°C.

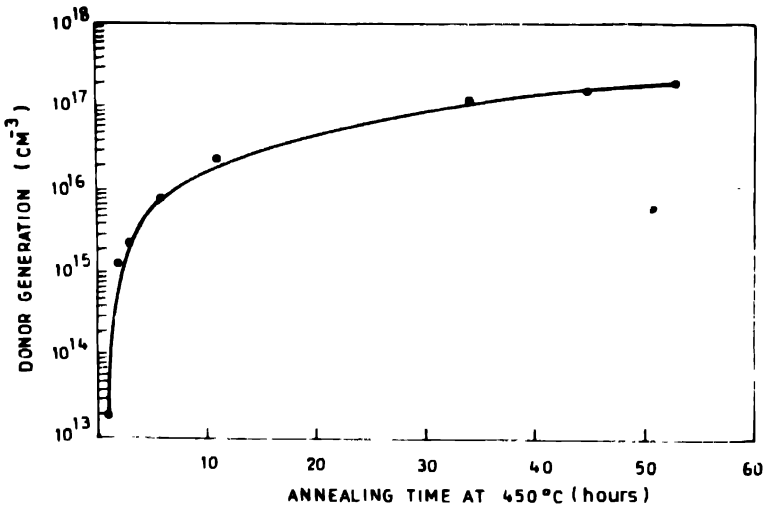


Figure 2. Donor generation vs annealing time at 450°C

later on. Our results are in agreement with Capper *et al* [10], Cazcarra and Zunino [11], Cleland [12], Kumar and Singh [13], and Mathiot [14]. The hole concentration in unannealed sample was found to be $1.2 \times 10^{14} \text{ cm}^{-3}$. Donor concentration was found to decrease in the early stage of annealing (upto 1 hour) but it increased exponentially as a function of annealing time later on. However, even for annealing times of 55 hours, the maximum in donor generation was not attained. As per trend of the curve at 55 hours, it

could be concluded that longer annealing durations would bring a saturation in donor concentrations.

Precise composition of the donor has been and still is a matter of debate. In his first ever model on the subject, Kaiser *et al* [15] assumed that in the 450°C region SiO_4 complexes are donors while those with more oxygen atoms are neutral. Some complexes with less than four oxygen atoms are also donors. They explained the maximum donor concentration as being the equilibrium between SiO_4 donors and neutral SiO_5 and SiO_6 complexes. The donor concentration falls after attaining a maximum of the annealing time is further increased. This result was explained by assuming that more SiO_5 and SiO_6 units are produced from SiO_4 units [15]. This model could satisfactorily explain the state of knowledge. Since then many models, varying in nature, have been put-forth. Silicon interstitialcy as nucleus and surrounded by O-atoms is more befitting.

3.2 FTIR results :

FTIR measurements, performed on two types of samples : one with high oxygen and carbon content and the other with moderate oxygen and carbon content, were used to determine absorption coefficients corresponding to 1106 cm^{-1} and 605 cm^{-1} respectively for oxygen and carbon in the un-annealed and annealed samples. A smooth and gradual decrease in the values of absorption coefficients of oxygen and carbon was noticed.

The fractional change of the IR absorption coefficient α_0 as a function of annealing time at 450°C is shown in Figure 3. Measurement of absorption coefficients at 1106 cm^{-1}

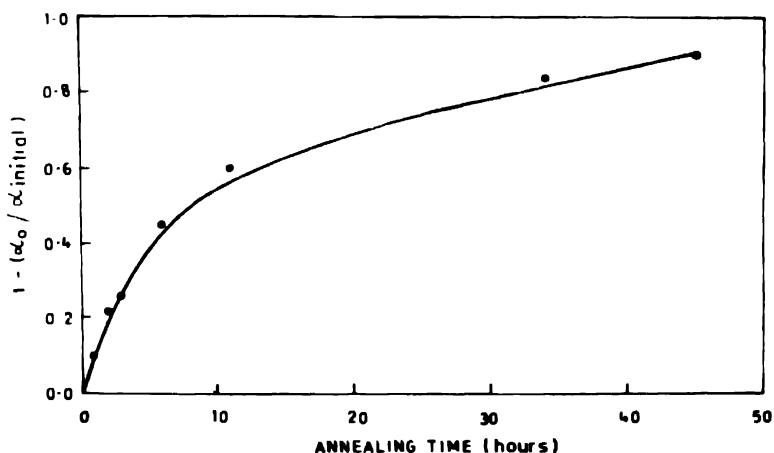


Figure 3. The fractional change of IR absorption coefficient as a function of annealing time at 450°C

reflected a decrease in isolated interstitial oxygen during annealing treatment. However, there is no direct way of measuring the fraction of oxygen precipitated, as a broad peak due to the precipitation, is superimposed on the 1106 cm^{-1} peak [16]. We also observed a weak and broad IR absorption peak at $\sim 1012\text{ cm}^{-1}$ in the FTIR spectra of annealed samples that

contain high concentration of thermal donors. This absorption may originate from Si-O vibration in cores of thermal donors.

3.3. Effect of carbon and ambient on donor formation :

Carbon and oxygen precipitation increased with increase in annealing time in our experiments [11]. Increase in the carbon precipitation with annealing time indicated a decrease in substitutional carbon concentration in annealed samples with increasing annealing time. In high carbon content samples, the donor formation was suppressed. This can be explained by the formation of stable CO complexes or oxygen precipitates, which resulted in the permanent lowering in the number of interstitial oxygen (O_i). Interstitial oxygen atoms expand the lattice whereas substitutional carbon atoms produce contraction. When both impurities are present, there is clearly a degree of strain compensation and there are direct infrared (IR) observations of C-O pairing, where the carbon atom is a nearest neighbour of the two Si atoms bonded directly to the O_i atom [17]. We also found that the ambient does not have any effect on the results as also opined by Bean and Newman [18]

3.4. Diffusivity of oxygen atom :

Differences of the reciprocal values of the actual oxygen concentration [$C(t)^{-1}$] and initial oxygen concentration [$C(o)^{-1}$] is plotted in Figure 4. A straight line is obtained suggesting

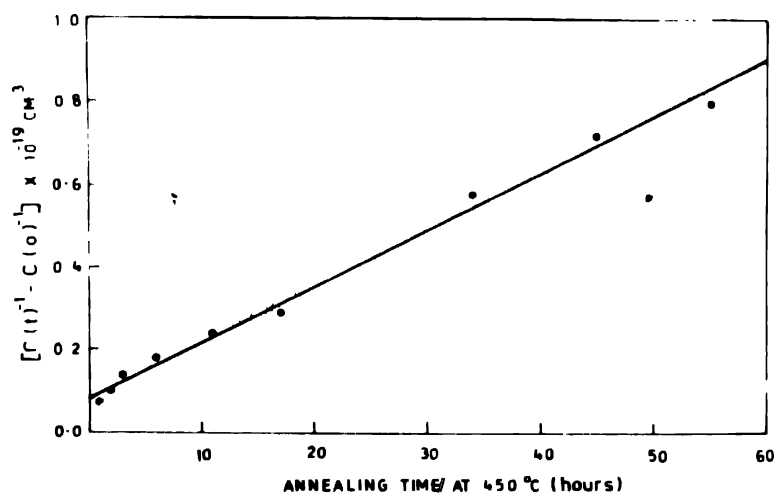


Figure 4. Plot of the differences of the reciprocal values of the actual oxygen concentration ($C(t)^{-1}$) and initial oxygen concentration ($C(o)^{-1}$) versus annealing time for $T = 450^\circ\text{C}$

that the oxygen reduction can be described by second order kinetics [19]. From the gradient of the straight line equal to $8\pi DR$, the diffusion coefficient D has been determined to be $\approx 4.17 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$. Here, R is the distance at which the oxygen atoms bind together to form a complex. $R = 5 \times 10^{-8} \text{ cm}$ was used in the calculation [20]. The value of D so obtained was substituted in the expression $D = 0.17 \exp(-E/kT) \text{ cm}^2 \text{ s}^{-1}$, which yields the

value of activation energy for the diffusion of oxygen to be 0.823 eV. Even lower activation energies for oxygen diffusion as compared to the above value, viz, $E_D = (0.7 \pm 0.2)$ eV was found [20] for annealing at temperatures between 525 and 600°C. This low activation energy can be explained by sinks of diffused oxygen, or more likely, by interactions of the diffused oxygen with that of other species like self-interstitial having a sufficiently high diffusivity at these temperatures.

3.5 Average number of oxygen atoms involved in a single TD :

From our experimental results, we have tried to find out the average number of oxygen atoms involved in a single TD. For this purpose, we took seven different samples of low carbon content and annealed these samples at 450°C for 55 hrs. By comparison between the number of donors generated and the amount of oxygen reduced, we found that it takes an average of about seven oxygen atoms for a single TD formation. There may be some loss of O_i due to the formation of carbon-oxygen complexes and also due to the formation of some oxygen related complexes (centres) that are no longer electrically active. However, we have tried to minimise the chances of forming carbon and oxygen complexes by taking low carbon content samples.

The average number of 7 oxygen atoms for a single TD formation is more logical as also opined by Lindström *et al* [21] and recently by McQuaid *et al* [22].

4. Summary

To get a glimpse of the outcome of the problem under consideration, we itemise the main findings of the present study as follows :

1. The resistivity of the sample increased initially upto 1 hour of annealing, then decreased exponentially suggesting that the sample changed from *p*-type to *n*-type for longer annealing duration due to the donor generation. Inhomogenities present in the sample got reduced after annealing.
2. Carrier concentration increased exponentially with increasing annealing time and became almost saturated for longer annealing times.
3. Oxygen precipitation can be described by second order kinetics. The activation energy for the diffusion of oxygen comes out to be ~0.823 eV.
4. Average number of oxygen atoms involved in a single TD comes out to be 7.

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